The Crystal Structure of the Cupric Complex with Succinimide. II. Potassium Tetrakis(succinimidato)copper(II) Hexahydrate and Lithium Tetrakis(succinimidato)copper(II) Monohydrate

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As part of a program for the study of the crystal structure of copper(II)-complex with succinimide, the crystal structures of potassium tetrakis(succinimidato) copper(II) hexahydrate and lithium tetrakis(succinimidato) copper(II) monohydrate have been determined by means of X-ray analysis. In the potassium-salt, the copper atom has a square planar coordination and the potassium ion has a trigonal prismatic environment formed by six oxygen atoms. In the lithium-salt, the copper atom has a flattened tetrahedral coordination, and each lithiun ion is tetrahedrally surrounded by four oxygen atoms. The conformational difference between the complex anion of the potassium-salt and that of the lithium-salt seems to result from the different sizes of the alkali-metal ions.

As part of a systematic study of the crystal structures of the copper(II)-complexes, crystal structure analyses of the $M_2(Cu(sucim)_4)nH_2O$ type, where M indicates an alkalimetal, have been planned to find the conformational features around the metals that might be responsible for the difference between the crystal structures of the complexes. The first investigation in this series was the crystal structure determination of $Cs_2(Cu(sucim)_4)2H_2O$.[1] In this paper, the crystal structures of $K_2(Cu(sucim)_4)6H_2O$ and $Li_2(Cu(sucim)_4)H_2O$ will be described.

Experimental and Structure Determination

*Potassium Tetrakis(succinimidato)copper(II) Hexahydrate.** Pink-colored crystals in the form of platelets were prepared by the method described by Tschugaeff.[2] Since the crystals effloresce easily in air, the crystals were sealed in glass capillaries for the X-ray work.

Preliminary Weissenberg and oscillation photographs showed the crystals to be triclinic; the crystal data are listed in Table 1.

For the 0kl–5kl layers about the *a* axis, intensity data were collected by the equi-inclination Weissenberg method with CuKα radiation. A large crystal with the approximate dimensions of 0.6×0.6×0.2 mm³ was used for the collection of the data, because the crystal of a suitable size for the X-ray work was consumed within one layer's exposure. Therefore, the data collected were not of a high degree of accuracy. A total of 1515 reflections was obtained, and the intensities were estimated visually with a standard scale. The usual Lorentz and polarization corrections were applied, but no correction was made for absorption and extinction. Corrections for variation in spot-size on the high-layer-line photographs were made by the method presented by Phillips.[3]

TABLE 1. CRYSTAL DATA

	Potassium-salt	Lithium-salt
Molecular formula:	$K_2CuC_{16}H_{28}N_4O_{14}$	$Li_2CuC_{16}H_{18}N_4O_9$
Molecular weight:	642.71	487.77
Crystal system:	Triclinic	Monoclinic
Space group:	$P\bar{1}$	$P2_1/a$
Cell dimension:	$a=8.51\pm0.03$Å	$a=24.61\pm0.02$Å
	$b=8.50\pm0.03$	$b=9.65\pm0.03$
	$c=9.28\pm0.02$	$c=8.58\pm0.02$
	$\alpha=97.4°\pm0.3°$	$\beta=94.4°\pm0.2°$
	$\beta=100.4°\pm0.2°$	
	$\gamma=79.9°\pm0.2°$	
Chemical units per unit cell:	1	4
D(calculated):	1.64 g/cm³	1.59 g/cm³
D(observed):	1.63 g/cm³	1.57 g/cm³

The space group was initially assumed to be $P\bar{1}$, implying a center of symmetry in the complex. The copper atom was placed at the origin of the unit cell, and approximate coordinates for the remaining atoms were obtained by Patterson synthesis and successive Fourier syntheses. The atomic positions and temperature factors were refined by a block-diagonal least-squares method. After several refinement cycles, the structure converged, with an *R*-value of 16%. The refinement with the $P1$ space group did not improve the *R* value and showed no tendency to destroy the center of symmetry. Thus, the space group was confirmed to be $P\bar{1}$.

All the atomic scattering factors were taken from the "International Tables for X-ray Crystallography."[4] Those of the copper and potassium atoms were corrected for anomalous dispersion, and anisotropic temperature factors were introduced for the copper and potassium atoms.

The final composite electron density and atomic parameters are shown in Fig. 1 and Table 2 respectively. The mean estimated standard deviations of the positional para-

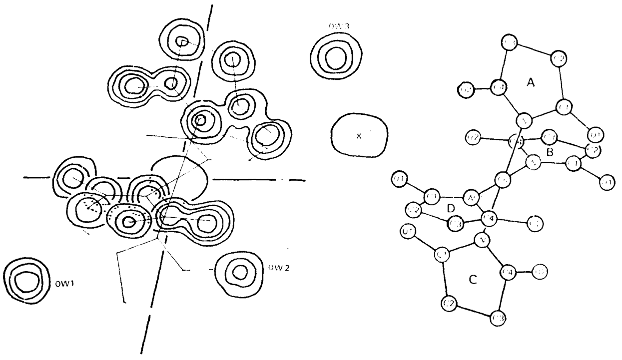

Fig. 1. The composite electron-density map and atomic numbering for $K_2(Cu(sucim)_4)6H_2O$. The contours are drawn at intervals of 2.0 e/Å³ starting at 0.5 e/Å³.

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* The term 'potassium-salt' will be utilized in this paper to describe this complex.

Table 2. Final atomic parameters of the potassium-salt

Atom	x	y	z	B	Atom	x	y	z	B
Cu	0.0000	0.0000	0.0000		K	−0.3971	0.1481	−0.0866	
OA1	0.2882	0.1756	0.1649	3.93	OA2	−0.2128	0.3160	0.0529	2.26
OB1	0.3555	0.0035	−0.1573	4.13	OB2	−0.1317	0.1497	−0.2928	2.56
NA	0.0391	0.2081	0.0969	0.89	NB	0.0874	0.0667	−0.1927	1.03
CA1	0.1574	0.2566	0.1676	1.43	CA2	0.1034	0.4285	0.2288	1.90
CA3	−0.0677	0.4773	0.1958	1.31	CA4	−0.0828	0.3277	0.1140	1.59
CB1	0.2305	0.0623	−0.2331	2.38	CB2	0.2859	0.1081	−0.3840	2.77
CB3	0.1265	0.1552	−0.4267	2.18	CB4	0.0161	0.1261	−0.3028	1.19
OW1	0.4384	0.3551	0.3648	3.71	OW2	−0.2808	0.3367	−0.4968	5.35
OW3	0.4580	0.4261	−0.1648	4.59					

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	0.0042	0.0021	0.0027	−0.0014	−0.0098	0.0019
K	0.0064	0.0050	0.0067	−0.0029	−0.0107	0.0048

Temperature factor $=\exp(-(h^2B_{11}+k^2B_{22}+hl^2B_{33}+hkB_{12}+hlB_{13}+klB_{23}))$
or $=\exp(-B(\sin\theta/\lambda)^2)$

Table 3. Final atomic parameters of the lithium-salt

Atom	x	y	z	B	Atom	x	y	z	B
Cu	0.1240	0.2090	0.2258		Li1	0.0488	0.0464	−0.0449	2.93
Li2	0.1403	0.4808	0.4491	3.87	OA1	0.0687	0.4033	0.4817	3.80
OA2	0.0073	0.0629	0.1452	2.57	OB1	0.1886	0.3489	0.5324	3.60
OB2	0.1393	−0.0908	0.3990	3.14	OC1	0.1166	−0.0461	−0.0149	3.03
OC2	0.2567	0.1799	0.2426	3.37	OD1	0.0565	0.2343	−0.1258	5.05
OD2	0.1419	0.5222	0.2208	2.95	NA	0.0510	0.2250	0.3052	2.22
NB	0.1562	0.1405	0.4324	1.63	NC	0.1774	0.0943	0.1226	2.19
ND	0.1066	0.3503	0.0632	2.26	CA1	0.0382	0.3104	0.4242	2.33
CA2	−0.0159	0.2620	0.4831	2.83	CA3	−0.0375	0.1559	0.3686	2.82
CA4	0.0073	0.1436	0.2634	2.23	CB1	0.1839	0.2180	0.5392	2.89
CB2	0.2114	0.1350	0.6713	2.96	CB3	0.1947	−0.0138	0.6300	2.65
CB4	0.1583	0.0069	0.4751	1.57	CC1	0.1630	−0.0185	0.0439	2.77
CC2	0.2072	−0.1285	0.0453	3.89	CC3	0.2571	−0.0420	0.1100	3.50
CC4	0.2311	0.0891	0.1599	1.62	CD1	0.0758	0.3440	−0.0663	3.21
CD2	0.0659	0.4768	−0.1452	3.74	CD3	0.0923	0.5811	−0.0275	5.21
CD4	0.1194	0.4823	0.0946	2.93	OW	0.1524	0.6573	0.5481	2.93

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	0.0006	0.0029	0.0042	0.0005	−0.0006	−0.0015

meters are 0.02 Å for the carbon, nitrogen, and oxygen atoms and 0.006 Å for the potassium atom.

Lithium Tetrakis(succinimidato)copper(II) Monohydrate.[**] Blue-colored, needle-like crystals were prepared by the same procedure as was used for the potassium-salt. Since the crystals were hygroscopic, the crystals for the X-ray work were sealed in glass capillaries. The crystals were monoclinic, with a space group of $P2_1/a$; the cell dimensions are shown in Table 1.

The intensity data were collected for the crystal ($0.05\times 0.40\times 0.05$ mm^3) rotating about the c axis, allowing the observation of 1869 independent reflections (l=0—6). The procedure of the determination of the structure was similar to that used in the case of the potassium-salt. The position of the copper atom was deduced from Patterson synthesis; a Fourier synthesis based on the phases determined by the copper atom revealed all of the non-hydrogen atoms except the lithium ions. The positions of the lithium ions were found by a difference Fourier synthesis. The refinement was carried out by the block-diagonal least-squares method; the final R value was 13%. The final atomic parameters are shown in Table 3. The estimated standard deviations of the

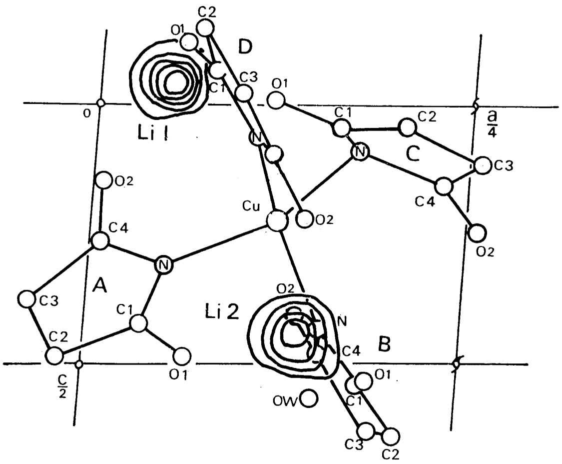

Fig. 2. The composite difference electron density map for Li$_2$(Cu(sucim)$_4$)H$_2$O. The contributions of the hydrogen atoms and lithium ions were excluded from the calculated structure factors. Two lithium ions are clearly shown in the map. The contours are drawn at intervals 0.05 e/Å^3 starting at 0.05 e/Å^3 for lithium ions, and there is no other peak higher than 1.2 e/Å^3.

[**] The term 'lithium-salt' will be utilized in this paper.

positional parameters are 0.05 Å for the lithium ions, 0.02 Å for the carbon, nitrogen, and oxygen atoms and 0.003 Å for the copper atom.

Results and Discussion

Geometry of the Coordination around the Copper Atom. In the present series of complexes, each of the copper atoms is coordinated by four nitrogen atoms from four succinimides. The bond lengths and angles around the copper atoms for the potassium- and lithium-salts are shown in Fig. 3.

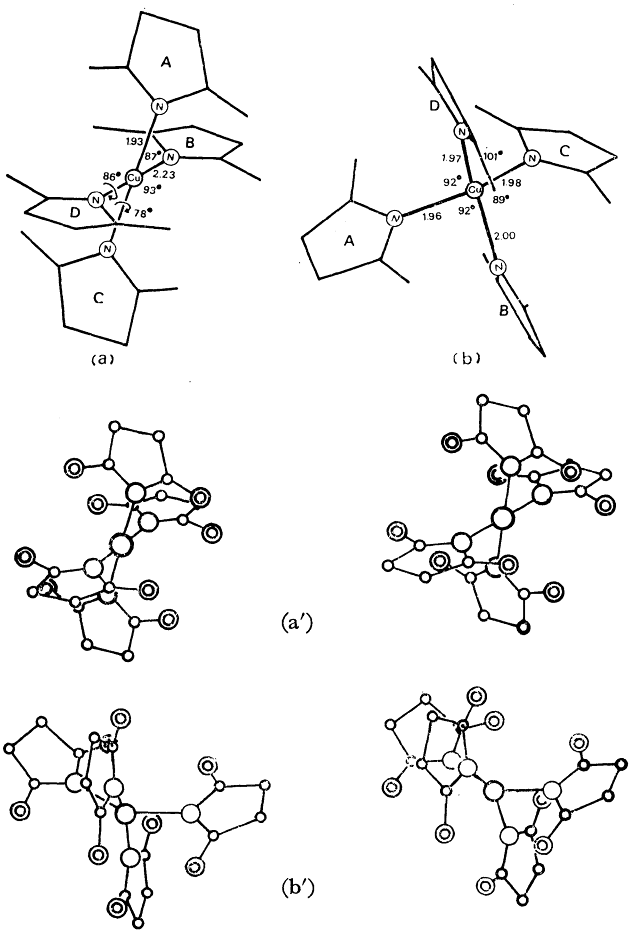

Fig. 3. The geometry around the copper atom.
(a) and (a′): Potassium-salt
(b) and (b′): Lithium-salt
(a′) and (b′) are the stereographic illustrations.

In the potassium-salt, the coordination around the copper atom is square planar and the complex anion is centrosymmetric. The coordination plane defined by the copper atom and four nitrogen atoms is, therefore, exactly planar. Although a distortion from an ideal square planar configuration may be evident in the different lengths of the Cu–N bonds and in the different angles of the N–Cu–N's, this can not be discussed in detail because of the low accuracy of the present analysis. Each plane of the succinimide residues is tilted by 82° to the coordination plane. Thus, the whole structure of the complex anion of the potassium-salt has a slightly distorted D_{4h} symmetry. This configuration for the anion agrees with that proposed spectroscopically by Yamada *et al.*[5]

In the lithium-salt, the coordination around the copper atom may be considered as either a distorted square planar or a distorted flattened tetrahedron. This configuration of the coordination resembles that of bis(*N*-ethyl-salicylaldiminato)copper(II) monohydrate[6] and that of 2,2′-biphenylbis(2-iminomethylenephenolato)copper(II).[7] The bond angles around the copper atoms in these complexes are listed in Table 4. Such a coordination polyhedron has generally been described as a tetrahedron distorted in the flattened form.

Table 4. Bond angles around the copper atom

Crystal I*		Crystal II*		Crystal III*
N(A)–Cu–N(B)	92°	O–Cu–N	93°	
N(A)–Cu–N(D)	92	O′–Cu–N	91	
N(B)–Cu–N(C)	89	O–Cu–N′	93	
N(C)–Cu–N(D)	101	O′–Cu–N′	94	
Average	94		93	92°
N(A)–Cu–N(C)	148	O–Cu–O′	152	
N(B)–Cu–N(D)	155	N–Cu–N′	157	
Average	152		155	152

* Crystal I, II, and III represent lithium tetrakis(succinimidato)copper(II), monohydrate, bis(*N*-ethylsalicylaldiminato)copper(II),[6] and 2,2′-biphenylbis(2-iminomethylenephenolato)copper(II),[7] respectively.

Environment of the Alkali-metal Ion. The distances around the alkali-metal ions are shown in Fig. 4. The mean distance from the alkali-metal ion to the oxygen atom in the individual complex is in fairly good agreement with the sum of their ionic radii: 3.11 Å for Cs–O, 2.71 Å for K–O, and 1.93 Å for Li–O respectively.

In the case of the potassium-salt, each of the K^+ ions is surrounded by six oxygen atoms at the corners of a distorted trigonal prism. One of these oxygen atoms belongs to the water molecule, while the remaining

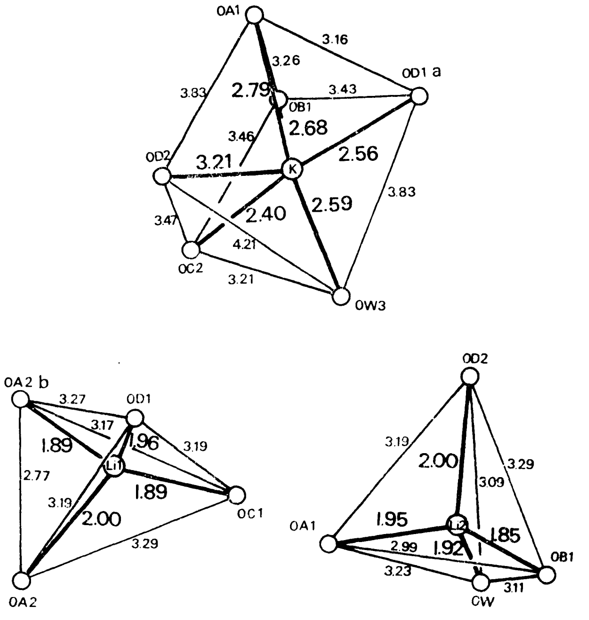

Fig. 4. The environment of the alkali-metal ion.

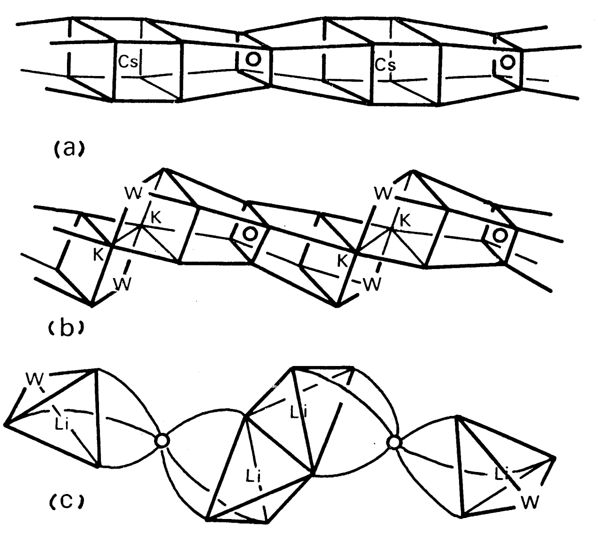

Fig. 5. The arrangements of coordination polyhedra around the alkali-metal ions in (a) cesium-salt, (b) potassium-salt and (c) lithium-salt. Circle and W represent the copper atom and the water oxygen atom, respectively.

five are the carbonyl oxygen atoms. Of these five carbonyl oxygen atoms, the four lying on the corners of a rectangular face of the prism, OA1, OB1, OC2, and OD2, belong to the same complex anion. Two trigonal prisms related to each other by a center of symmetry share an edge. Thus, an endless chain having the –A–K·K– sequence, where A indicates the complex anion and where K·K denotes two polyhedra sharing an edge, is formed. The chain formed by electrostatic interactions between the K^+ ions and the oxygen atoms is schematically shown in Fig. 5. The crystal structure consists of these chains held together by hydrogen bonds involving the water molecules.

In the case of the lithium-salt, two independent Li^+ ions exist in the structure. Both lithium ions have tetrahedrally-distributed oxygen neighbors; $Li(1)^+$ is surrounded by four carbonyl oxygen atoms, while $Li(2)^+$ has three carbonyl oxygen atoms and one water oxygen atom as neighbors. Of the eight carbonyl oxygen atoms in the complex anion, three coordinate to $Li(1)^+$, another three coordinate to $Li(2)^+$, and the remaining two are free. Such an arrangement of the carbonyl oxygen atoms with respect to the Li^+ ions may impose a large distortion from the D_{4h} symmetry upon the structure of the complex anion. Two tetrahedra related to each other by a center of symmetry are condensed by sharing an edge. The compositions of Li–A–Li·Li–A–Li, which are formed by electrostatic interactions between the Li^+ ions and the oxygen atoms, are linked together to form an infinite chain by the hydrogen bonds between the water molecules and the carbonyl oxygen atoms which are free from the Li^+ ions.

The crystal structures and the hydrogen-bonding schemes are illustrated in Figs. 6 and 7.

Consequently, it appears that the size of the alkali-metal ion may govern the structure of the complex.

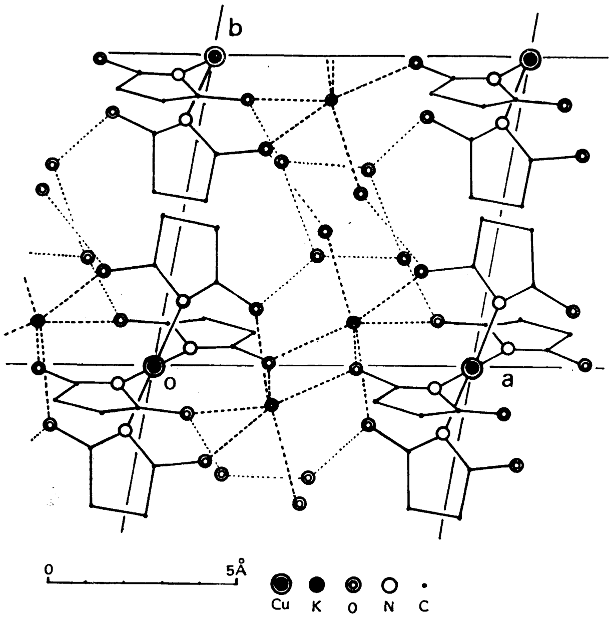

Fig. 6. The crystal structure of potassium-salt.

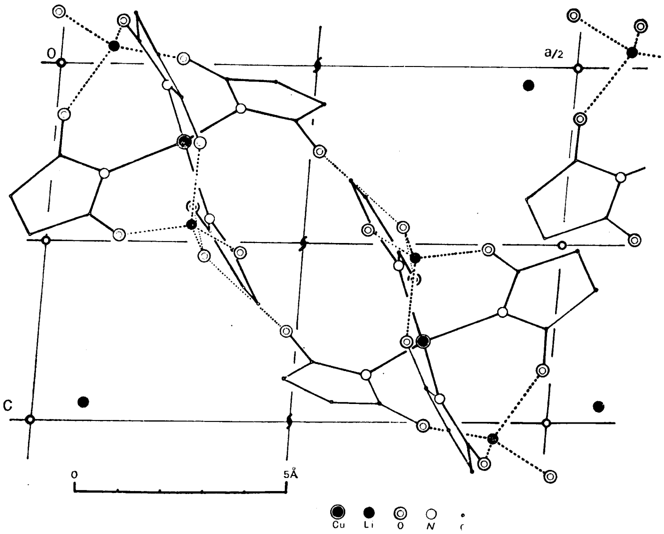

Fig. 7. The crystal structure of lithium-salt.

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References

1) T. Tsukihara, Y. Katsube, K. Fujimori, and T. Ito, This Bulletin, **45**, 2959 (1972).

2) L. Tschugaeff, *Ber.*, **39**, 2897 (1905).

3) D. C. Phillips, *Acta Crystallogr.*, **7**, 746 (1954).

4) "International Tables for X-ray Crystallography," Vol. III, Birmingham (1962), p. 202.

5) S. Yamada and S. Miki, This Bulletin, **36**, 680 (1963).

6) C. Panattoni, G. Borbieri, and R. Graziani, *Acta Crystallogr.*, **23**, 537 (1967).

7) T. P. Cheeseman, D. Hall, and T. N. Waters, *Proc. Chem. Soc.*, **1963**, 379.